

## **Molecule of the Year**

## Diamond: Glittering Prize for Materials Science

Its combination of properties, like its appearance, is absolutely dazzling. Diamond is the hardest substance known. It is inert to chemical corrosion and can

withstand compressive forces and radiation. It conducts heat better than any other material, has extremely high electrical resistance, and is transparent to visible light, x-rays, ultraviolet radiation, and much of the infrared spectrum. And, with respect to most of these features, diamond is superior to all other known materials.

Because of these outstanding properties, synthetic diamond materials—both crystals and thin films—that could be made cheaply would have great potential in research and commercial applications. Can they be produced? 1990 saw the start of the era in which this possibility could become a reality.

**Diamonds in the rough.** Before it was feasible to make synthetic diamonds, diamonds could only be obtained through mining, and never has there been what could be called a ready supply. Today, less than 20 tons of natural diamonds are mined each year throughout the world. Brazil, India, and South Africa have been, at different times, the world's major diamond-mining nations, though diamonds are also found in many other countries; today the Kaapvaal craton of southern Africa is one of the world's most productive diamond-mining centers.

Natural diamonds form in the earth's mantle in regions of high temperature and high pressure. Volcanic eruptions that originate from such regions bring diamonds to upper portions of the earth's crust in rocks known as kimberlites. Diamonds are mined from the conduits of the volcanos and from nearby placer deposits in stream beds and beaches.

The switch to synthetic. As new technologies have been developed for the production of artificial diamonds, the quest for diamonds has shifted more and more from the mine to the laboratory. The number of potential uses for diamond-based materials and the enormous profits anticipated have engendered an international race for high-quality artificial diamond production. Technologic breakthroughs for growing diamond materials and diamond films have come fast and furious in 1990. In addition, use of purer starting materials made possible the production of isotopically pure diamond films that have properties superior even to those of natural diamonds: the most exceptional of these is the extraordinary ability of the pure films to conduct heat. Although the cost of making synthetic diamond films with state-of-the-art chemical vapor deposition (CVD) methods is still high-estimated at around \$100 per carat-the price could drop significantly with the optimization of CVD technology.

**Applications.** A few diamond-based and diamond-coated products are already in use commercially—x-ray windows in electron microscopes, strong abrasion-resistant industrial tools, and diaphragms for tweeters in stereo speakers—but these represent only a tiny fraction of the anticipated applications. For hard-to-service, hard-to-reach environments where high pressures and temperatures, intense radiation, high salt content, and other adverse conditions can destroy materials (places like the ocean, space, engines, and nuclear reactors), fabrication of diamond materials and devices may be justified already, even at the currently high costs of production.

In both adverse and more standard settings, diamond substrates for semiconductors will be able to efficiently transport heat from electronic circuitry, obviating the need for cumbersome cooling systems. Because CVD diamond films have both high thermal conductivity and high electrical resistivity, the jewel in the crown of diamond film technology may well be superfast integrated diamond circuits. Diamond diodes (the building blocks of transistors, which, in turn, are the building blocks of integrated circuits) have recently been made. If successful doping of diamond can be accomplished routinely, diamond devices could someday replace silicon semiconductors. Whereas silicon chips can withstand temperatures up to 300°C, one estimate is that diamond chips might be able to withstand temperatures as high as 5000°C.

Doped single-crystal diamond films are needed for diamond semiconductors; for other applications polycrystalline diamond films are adequate. For example, abrasion-resistant tools are coated with this type of film. Industry faces a different sort of challenge with regard to these tools, namely determining what would be an equitable price to charge for saws and knives that never need sharpening or replacement.

Diamond thin films can be put on windows and lenses to make them scratch-proof, nonreflecting, and permeable to light. Because diamond films are wear-resistant, they might be fashioned into efficient, low-friction, unlubricated bearings for machinery and prosthetic devices. A megaproject that may be in the offing is the production of diamond films for use as high-speed detectors for the superconducting supercollider; it is predicted to involve more than a million carats of diamond film.

In addition to the production of diamond films and coatings, free-standing diamond materials are being fabricated. Diamond nozzles have been cast for use in diesel engines, and diamond sheets, domes, and tubes have been prepared on metal preforms.

Because the template is etched away, full advantage can be taken of diamond's extreme properties in the freestanding constructs.

The technological spadework. Interest in the production of artificial diamonds was expressed at the turn of the century, but it was not until 1958 that a method



was patented in the United States for preparing diamond materials from methane at high pressures and high temperatures (1600 K and about 55 kilobars). However, as the methane burned, graphite was also deposited, severely limiting the speed of diamond deposition and therefore the success of the process. (Both diamond and graphite are pure carbon materials, but the way that carbon atoms are organized in them differs: diamond is a rigid, dense, and essentially incompressible crystal in which tetrahedrally coordinated carbon atoms are linked in a cubic crystal lattice by covalent bonds; graphite is a soft material in which two types of bonds form to create a macrostructure of parallel sheets with hexagonal symmetry.)

In 1977, researchers in the Soviet Union found that deposition of the troublesome graphite could be prevented if excess atomic hydrogen were added to the reaction chamber. Hydrogen may both suppress formation of graphite nuclei and contribute to the creation of free radical sites. By 1981 the Russian scientists reported that they were able to form both single-crystal diamond films on diamond substrates and multiple diamond crystals on metal substrates.

**The film industry runs fast-forward.** With a solution to the graphite problem at hand, Japanese and other researchers began in the early 1980s to develop low-pressure CVD methods; these methods yielded high-quality single-crystal and polycrystalline films. With CVD, hydrogen gas is heated with a simple hydrocarbon compound such as methane (referred to in some of the popular accounts of the achievement as swamp gas, vodka, and sake) to temperatures of 2200°C. The carbon atoms are atomized and ionized and then rearrange and condense out onto the substrate. Diamond films made with CVD methods have proven to be both smoother and larger than those that could be made under high-pressure and high-temperature conditions.

In July of this year, scientists in the United States reported that isotopically pure diamond films (containing 99.9% carbon-12 and not the 1% carbon-13 that is present in natural diamonds) had been grown. The pure films not only conducted heat 50% better than the best natural diamonds but also withstood damage by laser radiation ten times more effectively than natural diamond.

Vapor deposition methodology now appears to be in an exponential phase of growth. Diamond films can be grown at pressures ranging from tens of torrs to 1 atmosphere. Film growth rates of 1 millimeter per hour are possible. Diverse volatilization methods have become available, including microwave discharges, hot filaments, plasma torches, and ion beams. The deposition of films at lower-than-normal temperatures (around 300°C instead of the standard 700 to 1100°C) has been accomplished through the addition of halogens to reaction mixtures; this is an important step if diamond is to be deposited on temperature-sensitive substrates. All of these variations on the basic CVD theme are making possible faster production of better materials with diverse morphologies.

For some purposes, diamond-like carbon films (which contain less than 1% hydrogen) or diamond-like hydrocarbon films (those with 20 to 60% hydrogen) may be as good or better than diamond films. In general, these films can be deposited at lower temperatures than can pure diamond films. The development of similar materials, such as the boron nitrides, may also benefit from the diamond technology boom.

The many facets of diamond film technology. Much has been accomplished with CVD technology even in the absence of a clear understanding of how and why this process transmutes hydrocarbon into diamond. Experimental and theoretical approaches are now coming together to provide an understanding of the kinds of intermediates that form during the deposition process, the specific molecular species that promote the growth of the crystal lattice, the types of atoms that bind to the crystal's edges, the impurities (nitrogen, boron, and others) that disrupt the formation of diamond crystals, the ways in which reaction conditions affect the speed of film deposition and film thickness and shape, and the means by which specific properties of films enhance their usefulness for various applications. Most materials—metals, ceramics, plastics, polymers, and paper—are considered desirable substrates for some application of diamond films, and so an understanding of what promotes bonding is critical. For some applications, epitaxial growth is required, whereas in other cases the substrate serves only as a form on which a film is fabricated.

It has taken a quarter of a century for artificial diamond film production to get under way, but, now that it has, the future for diamond-based materials is likely to be a gem.

## The Runners-up

There were many scientific and technological developments in 1990 that had their own exceptional sparkle. *Science's* top ten among these are described here.

**Terrific tesselations.** Distant cousins of diamonds, the 60carbon buckminsterfullerenes or buckyballs, can now be synthesized in bulk. The availability of gram-per-

day quantities of these soccer ballshaped all-carbon molecules is a real kick for chemists: it has already made possible many analyses of the structure, spectral signature, and properties of  $C_{60}$  that had not been possible before. This handle on buckminsterfullerenes should also facilitate measurements of the abundance of  $C_{60}$  in the cosmos. Such clusters are incredibly stable and, because candle burning, wood burning, and star burning



all create the conditions that favor formation of C<sub>60</sub>, the buckminsterfullerenes may turn out to be among the most abundant molecules in the universe. Buckminsterfullerenes have been attracting attention for about 5 years, ever since they proved to be surprisingly abundant vaporization products in experiments directed at the production of long-chain carbon molecules. Why are the buckyballs so much more stable than other poly-carbon molecules? All members of the fullerene family are stable because they have no dangling bonds; C<sub>60</sub> is the most stable of these complete hollow shells, perhaps because the way it curves minimizes stress on carbon-carbon bonds. The shape of the C<sub>60</sub> molecule immediately brings to mind several possible applications-as catalytic surfaces and as capsules for transporting small molecules through the body, as do vesicles and viruses which have similar shapes. Unmodified buckyballs react poorly with other substances and may, like their precursor graphite, be effective lubricants; if their surfaces can be modified (for example, with hydrocarbon chains), new forms of organic molecules could be created on buckyball frameworks.

**Juggled genes.** Gene therapy is in theory the way to attack inherited defects head on: substitute a normal gene for one that is malfunctioning or missing. The first human gene therapy experiments have now surmounted all political hurdles and are under way at the National Institutes of Health; how quickly enough of the technologic challenges can be met to make this therapy effective remains to be seen. Can the good gene be targeted to the right place and, in some cases, can the defective gene be removed at the same time? Can the genetically engineered cells be kept alive and functioning, and can they be made to reproduce? Will enough of the needed gene product be produced? Can all this be done without activation of "innocent bystander" oncogenes inside the therapeutic cell? The genetic disease that was chosen for the prototype gene therapy trials is the immunodeficiency caused by an adenosine deaminase (ADA) deficiency. The disease would appear to be a

perfect choice in which to evaluate and improve gene therapy technology. It is caused by a simple genetic deficiency-one enzyme is missing-and therefore might also be "simply" corrected. Although the disease affects perhaps no more than 50 people around the world, it is nonetheless widely known because of the poignant image projected by the "Boy in the Bubble." People born with an ADA deficiency cannot fight infectious diseases; they either live in a sterile (bubble) environment or are continually sick, and they die young from overwhelming infections. Cells carrying a functional gene for ADA have been given to the first few pioneer patients, but it is still too soon to evaluate the efficacy of these trials. Cystic fibrosis is also high on the gene therapy list; it is the most common fatal genetic disease in Caucasians in North America. Last year the gene that is responsible for cystic fibrosis was identified. This year, the faulty cystic fibrosis genes in two types of cells in culture were replaced with their normal counterparts; the substitution repaired defects in the cells' membrane ion channels, preventing the cells from swelling. It remains to be seen whether cells repaired in this fashion can reverse symptoms brought on by the build-up of dry mucus in the lungs of cystic fibrosis patients.

**No-show neutrinos.** Detection of solar neutrinos that are produced by fusion reactions in the sun's core is the only direct way to confirm that nuclear fusion is what causes the sun to shine. About 2% of the sun's energy is thought to be emitted as neutrinos; the rest as heat and light. The detection of solar neutrinos has not been a simple matter because they are low in energy, have no charge and little or no mass, move at the speed of light, and are not stopped by trivial barriers (like the earth). Nonetheless, for the past 23 years, the interactions of the higher energy solar neutrinos with an isotope of chlorine have been monitored in a vat at the Homestake Gold Mine in South Dakota. From these underground measurements, the "solar neutrino problem" has surfaced: only a third or a fourth of the number of neutrinos expected on the basis of standard solar models is detected. Is the shortfall due to a faulty detector, incorrect formulation of the physics of the sun, or a misunderstanding of

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neutrino physics? Last year the Japanese Kamiokande II detector confirmed the neutrino deficit; it also tracked the path of the neutrinos and showed that the neutrinos were indeed coming from the sun. This year, two gallium-based detectors (the joint Soviet-American SAGE detector and the Italian Gallex detector) are joining the search for solar neutrinos. The gallium detectors can

detect lower energy neutrinos and thus should be able to monitor the vast majority of neutrinos coming from the sun, those produced by proton-proton fusions. Measures of the sun's brightness and of the neutrino flux should jibe; if they do not, and so far they have not, new neutrino physics will be in order. The new physics could include a mass for neutrinos and oscillations and transmutations between the three different types of neutrinos—electron, muon, and tau—while they are still inside the sun.

Alluring aerogels. Aerogels are strong, light, airy materials. The most airy aerogel prepared to date consists of 99.8% air; the rest is

silicon dioxide. So far aerogels have been used only in high energy physics particle detectors. However, their properties they do not conduct heat or sound well, they refract light, and they are almost transparent—have suggested uses for



them as insulators in refrigerators, buildings, and windows. Half an inch of a silica aerogel can do what it takes  $3^{1}/2$  inches of a fiberglass insulator to do. Aerogels are being evaluated for use in space research to capture unharmed, fast-moving particles. The preparation of an aerogel begins with the preparation of a gelatinous polymer. High pressures combined with high temperatures are then used to remove the liquid from the gel in such a way that surface tension is not created: the fluid enters a supercritical state (gas and liquid are physically the same) and the gel does not collapse in on itself. Air moves in as the fluid moves out and what remains is an airy mesh, a kind of solid smoke.

Powerful pills. Well over half a million Americans are currently taking the drug Prozac in order to control depression and other common psychological disorders, including anxiety, obsessivecompulsive behaviors, and bulimia. So far, Prozac is acting as something of a wonder drug; it is highly effective, causes few dangerous side effects, and is already the most widely prescribed antidepressant after just 4 years on the market. Prozac and earlier generations of drugs for depression (the tricyclics and the monoamine oxidase inhibitors) are not only changing the clinical outlook for depressed individuals but are providing valuable clues to the electrochemical circuitry of the brain and to how such circuitry might be modified in psychiatric diseases and in mental disorders. Depression has been associated with abnormally low activity of neurotransmitters, one of which, serotonin, appears to be Prozac's target. Normally, serotonin is released by a nerve cell, crosses a synapse to bind to a receptor on a second nerve cell, and then activates the second cell; later, serotonin is released by the second cell and is either degraded in the synaptic cleft or reabsorbed by the cell that originally secreted it. Prozac seems to block the reuptake of serotonin by the first cell. Because serotonin stays in the cleft longer, it also can work longer. Many pharmaceuticals besides Prozac have proved their worth in modulating neurologic functioning; two good examples are L-DOPA and Ritalin. Drug receptors can often be discovered with conventional biochemical techniques; thus, in addition to the therapy they provide, psychoactive drugs (like a range of imaging techniques) are of value for associating activity with architecture and are helping to map specific mental activities to specific regions of the brain.

Twinkling tweezers. Sperm that are too weak to penetrate the

protective coat around an egg may soon be helped by laser beams. Femtosecond laser pulses can make tiny puncture holes in the egg's zona, thereby permeabilizing this protective layer so that the sperm can push their way through to the egg. Many advances in laser technology during the past 30 years have contributed to the production of the new precision lasers that act like mini-tweezers, mini-scissors, and mini-scalpels, catching, trapping, puncturing, cutting, and splicing subcellular structures and pushing or pulling them from place to place. The new laser tools have been used for a number of biomedical and biological projects-clipping off regions of chromosomes (followed by assessments of the consequences of the loss to the cell), cutting and splicing membranes, and moving organelles around inside cells. Chemists and physicists are using the advanced lasers to study molecular behavior by "pushing" molecules tiny distances within crystals; they have also harnessed the energy of lasers for splitting and ionizing molecules that participate in simple chemical reactions and have confirmed quantum mechanical predictions of simple reaction dynamics.

**Growth industry.** Everyone's favorite bacterium, *Escherichia* coli, is now churning out bovine growth hormone in quantities that put the pituitary glands of cows to shame. "Bovine somatotropin" is expected to be one of the next products of recombinant DNA technology to reach the marketplace; at the threshold, it is encountering a variety of obstacles. The hormone has powerful effects on lactation and can increase milk yields by as much as 25% per cow. Dairy lobbies in both the United States and Europe are troubled that the already precarious existence of small farmers will be further jeopardized if this new product is approved and large producers garner an even greater share of the market than they already control. Two states, Minnesota and Wisconsin, have for the time being banned the sale of the recombinant hormone; so has the European Parliament. There are also safety issues involved. Is the hormone safe for treated animals? Bovine somatotropin causes organ enlargement

and lower reproductive rates in treated animals. Is there a possibility that the hormone will be dangerous to human consumers? Available evidence (published in the 24 August 1990 issue of *Science*) indicates that the health risk to human consumers is negligible. Sometime next year when all the data are in from multi-year animal-

safety studies, the U.S. Food and Drug Administration will decide whether to approve the product for commercial use. Because of the continuing controversy, the National Institutes of Health also has convened a consensus panel to assess the animal and human safety of bovine somatotropin.

Gigantic gene. In July, the gene for type 1 neurofibromatosis or Von Recklinghausen disease was cloned. The disease affects about 1 person in 3000, so its incidence is less than that of cystic fibrosis or sickle cell anemia in American blacks. The most common signs are benign but extremely disfiguring tumors (called neurofibromas), cafe-au-lait (patchy) spots on the skin, and nodules on the iris. In a number of cases, learning disabilities, malignancies, and various neurologic manifestations also occur. The NF-1 gene is huge and is thought to have as many as two million base pairs. At least three other genes are embedded in NF-1, piquing interest in whether these passenger genes have a role in the disease process. NF-1 is highly conserved, which suggests that under normal conditions it may have some important cellular function. When the sequence of NF-1 was compared with sequences of 20,000 other genes, striking homology was found with portions of two others. Current thinking is that the three homologs are tumor suppressor genes. Tumor

suppressors keep cells from engaging in runaway proliferation, but when they are mutated their hold on the cell is broken and tumors can arise. The possible association of the *NF-1* gene product with tumor suppression has excited researchers studying all types of human cancers, because the molecular mechanisms that trigger Von Recklinghausen disease may be similar to those that initiate other human tumors.

Magical motifs. Molecular biologists have made significant progress this year in clarifying some of the complex interactions of protein and DNA molecules that result in gene activation. Differential gene transcription, the turning on and off of specific genes, is what ensures that, for example, a developing heart cell will in fact grow and differentiate into a heart cell despite the presence of all the genes necessary to make it a liver or stomach cell. Although many different types of transcription factors have been identified and studied in both simple and complex organisms, structural studies now indicate that the factors can be sorted into just a few categories on the basis of their conformations. Two distinct "motifs" are prevalent among the many transcription factors and appear to mediate the formation of dimers that then bind to DNA. One motif is the leucine zipper; the other is a helix-loop-helix arrangement. Both are typically situated close to highly positively charged regions of amino acids that interact with negatively charged DNA. "Partnering" has recently been observed to occur between dissimilar transcription factors. This increases the diversity of transcriptional activating complexes that can be generated within a cell. Thus, from a relatively small number of transcription factors, many distinctive dimers can form; each can have a new specificity, new binding affinity, and new effect on gene expression.

**Cosmic questions.** The field of cosmology, which has long been rich in theory, is now growing rich in data as well. A striking example of the new wealth is the data returned this year by the Cosmic Background Explorer satellite (COBE), which was launched by the National Aeronautics and Space Administration in November 1989. COBE is examining the "afterglow" of the Big Bang—the photons that were emitted within a few hundred thousand years of the event. Ground-based observations of the cosmic background radiation have shown it to be homogeneously distributed; in COBE's first few minutes of observation, its infrared absolute spectrophotometer confirmed at high resolution that the spectral signature of the

afterglow was that of a perfect black body. The COBE measurements are addressing two related cosmologic mysteries: why is the cosmos, overall, so homogeneous, and how did structure



(stars, galaxies, clusters, superclusters) evolve out of the smooth background? The COBE instruments continue the search for the tiny seeds of inhomogeneity that are thought to be the foci around which the first stars would have formed; within a few months, these measurements should reach a level of resolution of one part in  $10^5$ . When the expected fluctuations are found, existing theories that account for the appearance of structure will need some refinement. If the fluctuations do not appear, theorists will be back at square one looking for new energy sources to invoke along with the Big Bang to account for the formation of the universe.

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